Hierarchical refinement of complex microkinetic models

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Introduction

Microkinetic modeling of heterogeneous catalysis is becoming quite rapidly a widely applied technique for the analysis and design of catalytic processes. Such models are quite attractive and useful since in principle, differently from classical kinetics, they do not require a priori assumptions on the rate determining step(s) and can capture the reacting system behavior under significantly different operating conditions. Key in this respect is the achievement not only of a quantitative description of the experimental data, but also of the consistency between the predicted catalytic cycle and the macroscopic kinetic behavior (e.g., global reaction orders) [1]. Such envisioned reliability of the model poses severe challenges for the development. This is particularly true for complex system of real technological interest, where an exhaustive and unbiased description of the elementary steps is unfeasible due to the large number of steps and the intrinsic limitation of the model description. To overcome these limitations and to make possible the development of physically sound microkinetic models, different and comprehensive information on the kinetic parameters are needed and in particular have to be harmonized through a hybrid and hierarchical approach [2]. In the context of this work, we present a hierarchical refinement of the microkinetic model by Maestri et al. [2] for the description of CH_4 conversion on Rh. The DFT-refined description of WGS/RWGS pathways by Maestri and Reuter [1] is introduced in the microkinetic model and refinement of reaction parameters is carried out based on a comprehensive set of isothermal experimental data.

Methodology

The hierarchical data-driven approach by Maestri et al. [1, 2] is used in order to introduce in the microkinetic model the information derived from first-principles calculations [1]. At this scope, we used a comprehensive set of experimental tests performed in an annular reactor, including methane CPO, steam reforming, WGS, RWGS and COx methanation. We identified the dominant reaction mechanism through reaction path analysis (RPA) and compare it with selected experiments. Reaction parameters were modified within the order of uncertainty in order to obtain qualitative (e.g., observed reaction orders) and quantitative agreement with experimental data.

Results and Discussion

Starting from the first-principles analysis reported in [1], the elementary steps of the microkinetic model have been accordingly modified and assessed against a wide range of conditions and reacting systems (WGS/RWGS, steam and dry reforming, CO/CO_2 methanation, CPO).

Figure 1 shows a comparison between water-gas-shift (WGS) experimental data (symbols) and predictions of the original (dashed line) and revised (continuous line) models. Prior the modification reported in [1], the model was not able to correctly reproduce the behavior of the WGS system and resulted much faster in approaching equilibrium than what was experimentally observed. In terms of predicted reaction pathways, the conversion of CO to CO_2 was due the direct conversion via OH (CO+OH => CO_2 + H). On the basis of the first-principles analysis of [1], we removed the direct oxidation of CO to CO_2 via OH from the microkinetic model and optimized again the parameters as outlined in [2]. Such a modification led to a consistent improvement of the model performances both in terms of quantitative predictions and in terms of identified reaction pathways (i.e., reaction orders). Such an improvement on the description of the WGS reaction provided also peculiar insights in the analysis of experimental data of CPO, reforming and methanation experiments. For instance, the effect of the modification of the WGS description on the adiabatic partial oxidation of CH_4 is presented as Figure 2. In particular, the original model predicted an overshoot of CO_2 that was not experimentally observed, due to the fast approach to equilibrium of WGS system. Such a discrepancy was completely recovered with the new description of WGS derived from the first-principles analysis [1].

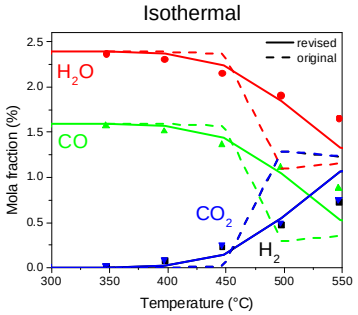

Figure 1. Comparison between experimental data (symbol) and predictions of the original (dashed lines) and revised (continuous lines) models for isothermal test of WGS.

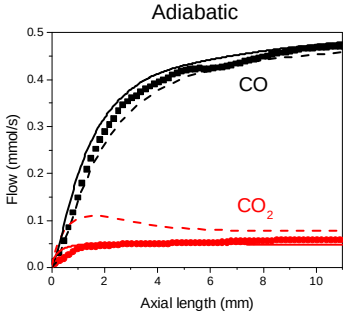

Figure 2. Comparison between experimental data (symbol) and predictions of the original (dashed lines) and revised (continuous lines) models for adiabatic run of CPO [3].

Significance

This work provides a clear show-case of the complexity of the development of a microkinetic model. In particular, all the information on the kinetic parameters of the elementary steps need always to be harmonized and tested not only with respect to the quantitative description of experimental data, but also with respect to the prediction of the underlying catalytic cycle.

References

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